

PATENT ABSTRACTS OF JAPAN

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(54) PRODUCTION OF BROMINATED POLYSTYRENE

(57) Abstract:

PROBLEM TO BE SOLVED: To provide a method for producing a brominated polystyrene which has a good color tone and has a high bromine content, in good productivity without generating a gel.

SOLUTION: This method for producing a brominated polystyrene comprises subjecting a 11-30 wt.% solution of polystyrene having a number-average mol.wt. of 10,000-30,000 and a mol.wt. distribution of 1.0-3.0 in a halogenated organic solvent to a bromination reaction using bromine or chlorine bromide in an amount of 2.0-4.5 moles per mole of the styrene skeleton unit of the polystyrene in the presence of a Lewis catalyst.

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CLAIMS

[Claim(s)]

[Claim 1] The manufacture approach of bromination polystyrene that number average molecular weight is characterized by for 10,000-30,000, and a molecular weight distribution mixing a 2.0-4.5-mol bromine or bromination chlorine with the solution which dissolved the polystyrene of 1.0-3.0 in the halogen system organic solvent by 11 - 30% of the weight of concentration under existence of a Lewis acid catalyst to one mol of styrene frame units of this polystyrene, and performing a bromination reaction.

[Claim 2] The manufacture approach of the bromination polystyrene according to claim 1 which is the catalyst which the Lewis acid catalyst consisted of metal aluminum 0 - the 100 weight sections to a kind of compound chosen from the group which consists of an aluminum chloride, aluminium bromide, and 3 ferric chloride, and the this compound 100 weight section at least, and passed the screen of 32 micrometers of apertures.

[Claim 3] The manufacture approach of bromination polystyrene according to claim 1 that a halogen system organic solvent is dichloromethane, chloroform, bromoform, bromochloromethane, 1,1-dichloroethane, 1,2-dichloroethane, 1,1,1-trichloroethane, or bromoethane.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the manufacture approach of bromination polystyrene. In more detail, it excels in productivity and bromine content is related with the manufacture approach of the good high bromination polystyrene of a hue.

[0002]

[Description of the Prior Art] As for bromination polystyrene, two kinds of manufacture approaches are indicated fundamentally. The approach of one of them brominating a styrene monomer and carrying out the polymerization of this and other one are the approaches of brominating polystyrene. For example, as a former example, on the German JP,1544694,B specifications, a styrene monomer is brominated and the approach of carrying out the polymerization of the monomer obtained successively is indicated. However, the process which manufactures the bromination styrene monomer which is a raw material is required of this approach, a price becomes high, and the polymerization reaction itself needs strict management on a process, there is a fault, like further, it is difficult to make a bromine content increase and it becomes in transit [the fire-resistant engine performance as a flame retarder], and it is hard to call it a desirable approach.

[0003] The approach which is partly indicated as a latter example, for example, brominates a styrene monomer after a polymerization by JP,53-60986,A on the other hand is shown. However, in case the bromination polystyrene from which the range of the approach of starting is specifically 800-8000, and the mean molecular weight of a styrene polymerization product is obtained contains a residual monomer or oligomer, and neither a hue nor thermal stability is enough, scours this bromination polystyrene to resin and fabricates, the problem of occurring may generate metal mold contamination.

[0004] Moreover, after dissolving polystyrene in a solvent, in the approach of brominating under catalyst existence, by JP,56-129202,A, bromination of the polystyrene of a low degree of polymerization is indicated, it is shown concretely that a degree of polymerization uses the thing of 6-200 suitably, an osmolarity determination is described by the specification as the measuring method by it, and it is thought by it that substantial number average molecular weight is 400-8000. That is, it can be understood as the polystyrene of the molecular weight which contained styrene oligomer like the above-mentioned official report.

[0005] Furthermore, after dissolving polystyrene in a solvent, in the approach of brominating under catalyst existence, by JP,54-100492,A, the average molecular weight of the polystyrene used suitably is described to be the range of 50,000-500,000, and, specifically, brominating the polystyrene of molecular weight 150,000 with the dichloromethane solution of concentration 25% of the weight is shown by it. However, there are few additions of a bromine in this case, and the bromine content of the obtained bromination polystyrene is as low as 61.5%.

[0006] moreover, after dissolving polystyrene in a solvent on U.S. Pat. No. 5723549 number specifications, in the approach of brominating under catalyst existence, about the molecular weight of polystyrene, weight average molecular weight is described to be the range of 500-1,500,000, and there is no substantial limitation -- it is alike and equal. The polystyrene of weight average molecular weight 300,000 is brominated with the 1,2-dichloroethane solution of concentration 10% of the weight, and, specifically, having obtained the bromination polystyrene which has 66% or more of high bromine content is shown.

[0007] On the other hand, conventional usual polystyrene is used, when it faces obtaining the high bromination polystyrene of bromine content and brominates with a high concentration solution, the system of reaction needs to serve as gel, the bromination reaction in a high concentration solution needs to become difficult substantially, a low concentration solution needs to perform a bromination reaction, and there is a problem that productivity falls.

Moreover, if solution viscosity rises very much even if it is in a dissolution condition, being spread [of a bromine] becomes inadequate, for this reason the permutation to a principal chain or formation of an unsaturated bond occurs in addition to the bromination to a ring, and in case hot forming of this bromination polystyrene is blended and carried out to resin, coloring and generating of inorganic bromine system gas will take place.

[0008] Therefore, a hue is good and a method of manufacturing the high bromination polystyrene of bromine content with sufficient productivity is desired.

[0009]

[Problem(s) to be Solved by the Invention] The hue of this invention is good and it aims at offering the approach of manufacturing with sufficient productivity, without gelling the high bromination polystyrene of bromine content. Even if the solution concentration of raw material polystyrene was high concentration, gelation did not take place, but this invention person reached [that the good bromination polystyrene of a hue with high bromine content is obtained with sufficient productivity, and] a header and this invention, when a bromination reaction was performed using the polystyrene which has specific number average molecular weight and a specific molecular weight distribution, as a result of attaining the above-mentioned purpose and repeating examination wholeheartedly.

[0010]

[Means for Solving the Problem] That is, according to this invention, a 2.0-4.5-mol bromine or bromination chlorine be mix with the solution with which 10,000-30,000, and a molecular weight distribution dissolved [number average molecular weight] the polystyrene of 1.0-3.0 in the halogen system organic solvent by 11 - 30% of the weight of concentration under existence of a Lewis acid catalyst to one mol of styrene frame units of this polystyrene, and the manufacture approach of the bromination polystyrene characterize by perform a bromination reaction be offer.

[0011] the polystyrene used as a raw material by the manufacture approach of this invention -- number average molecular weight -- 10,000-30,000 -- desirable -- 11,000-25,000 -- it is -- and the molecular weight distribution -- 1.0-3.0 -- it is polystyrene of 1.0-2.8 preferably. This polystyrene is compoundable by various kinds of approaches, such as a radical polymerization, anionic polymerization, and cationic polymerization. Here, number average molecular weight and molecular weight distribution (weight average molecular weight/number average molecular weight) are measured with steric exclusion chromatography, and are searched for.

[0012] With [the number average molecular weight of raw material polystyrene] 10,000 [less than], probably because the structure of bromination polystyrene is unstable, the hue of the obtained bromination polystyrene gets worse, and the amount of generation of gas at the time of heating becomes large and is not desirable. If number average molecular weight exceeds 30,000, the rise of the solution viscosity of reaction mixture becomes extremely, operability will fall, gelation will take place further, and it will be inferior to productivity, and is not desirable, and it becomes difficult and is not desirable for advance of the reaction in the uniform condition of polystyrene and a bromine to be barred, and to obtain the high bromination polystyrene of the target bromine content. or [moreover, / that gelation takes place to bromination reaction time since many low molecular weight constituents or amount components of macromolecules are contained when molecular weight distribution exceed 3.0] -- or the hue of the obtained bromination polystyrene gets worse and is not desirable.

[0013] Although the technique of the usual aromatic series nucleus bromination is used about a bromination reaction, as a solvent to be used, the halogen system organic solvent which is inactive is used to a bromine and a catalyst. As this halogen system organic solvent, dichloromethane, chloroform, bromoform, bromochloromethane, 1,1-dichloroethane, 1,2-dichloroethane, 1,1,1-trichloroethane, bromoethane, etc. are mentioned, and dichloromethane and 1,2-dichloroethane are desirable. these solvents are independent -- or two or more sorts can use it, mixing. Although the solvent usually used for a reaction is an anhydrous solvent in order not to carry out deactivation of the catalyst, you may be the solvent which carried out dehydration processing of the recovery solvent, and was substantially changed into the anhydrous condition.

[0014] It is the solubility to the above-mentioned solvent that the number average molecular weight and molecular weight distribution of polystyrene affect it, and with the polystyrene with which are not satisfied of the number average molecular weight and molecular weight distribution of polystyrene which are used by this invention, the upper limit of the solution concentration of bromination reaction time is about 10 % of the weight, and with the concentration beyond it, a reaction solution cannot serve as gel at bromination reaction time, and it cannot perform a uniform reaction substantially. By the manufacture approach of this invention, even if the solution concentration of the polystyrene of bromination reaction time is 13 - 25 % of the weight more preferably 12 to 28% of the weight 11 to 30% of the weight and performs the bromination reaction of the above-mentioned polystyrene by the solution concentration of this range, the viscosity of a reaction solution is suitable, gelation does not take place, but a reaction occurs in homogeneity and operability and productivity become good. It becomes [the viscosity of a reaction solution becomes extremely high,

or / gelation takes place and / a reaction] uneven and is not desirable, if the productivity of bromination polystyrene falls at less than 11 % of the weight and the solution concentration of polystyrene exceeds 30 % of the weight preferably.

[0015] A bromine or a bromine chloride is used as a brominating agent used in the manufacture approach of this invention. These may be used as a solution which dissolved in the above-mentioned halogen system organic solvent. These brominating agents are used for the substitution reaction to the ring of polystyrene, and the 2.3-4.4 mols of the 2.4-4.2 mols of the amount used are 2.5-4.0 mols especially preferably more preferably preferably [2.0-4.5 mols] to one mol of styrene frame units of the polystyrene of a raw material. By using the brominating agent of this range, bromination polystyrene of 65 - 68 % of the weight of bromine content considered as a request can be obtained. If this brominating agent is used superfluously, the product from which gelation becomes easy to take place, and was obtained by bromination reaction time colors remarkably and is not desirable, either.

[0016] Especially as an approach of mixing a polystyrene solution, a bromine, or a bromine chloride, it is not limited, but a reaction is stabilized by the approach of trickling a bromine or a bromine chloride gradually into a polystyrene solution, it advances, and it is adopted preferably.

[0017] The catalyst used in the manufacture approach of this invention is the usual Lewis acid catalyst, and the catalyst which consists of metal aluminum 0 - the 100 weight sections is preferably used to a kind of compound chosen from the group which consists of an aluminum chloride, aluminium bromide, and 3 ferric chloride, and the this compound 100 weight section at least. An aluminum chloride is desirable especially. Here, the metal aluminum used by request reacts with the bromine of the system of reaction, substantially, it may have denaturalized to the aluminium bromide, the chlorination aluminium bromide, or chlorination iron bromide aluminum complex, and there is an inclination which catalytic activity increases by addition of metal aluminum. When you do not need the increment in catalytic activity, you may advance a reaction, without adding metal aluminum. Therefore, metal aluminum can be added afterwards and the condition of a bromination reaction can also be controlled by the situation of the system of reaction. As for this Lewis acid catalyst, it is desirable that the diameter is powder 32 micrometers or less, and it is acquired by sifting out with the screen of 440 meshes (32 micrometers of apertures) under a desiccation ambient atmosphere simple. It becomes [the hue of the bromination polystyrene which the deactivation reaction at the time of catalyst deactivation after a bromination reaction was smoothly performed as the diameter of this catalyst is 32 micrometers or less, and was obtained] good and is desirable.

[0018] A bromination polystyrene solid-state can be obtained from the bromination polystyrene solution obtained by the manufacture approach of this invention by adding the solution concerning a well-known approach, for example, warm water, or a boiling water, and since recovery of a solvent can carry out to coincidence, this approach is adopted preferably.

[0019] The bromination polystyrene obtained by the manufacture approach of this invention has a good hue, it is excellent in thermal stability, it is suitably used as a flame retarder of polyester resin, such as polyamide resin for which the processing especially in an elevated temperature is needed, polyethylene terephthalate, and polybutylene terephthalate, and can give the good flame-retardant-resin constituent of a hue.

[0020]

[Example] Although an example is raised to below and this invention is explained in full detail, this invention is not limited to these examples. In addition, measurement of the various properties in an example was performed by the following approaches.

[0021] (1) Using HPLC measuring device LC-10A (Shimadzu make) equipped with GPC column KF[by number average molecular weight and molecular-weight-distribution measurement Showa Denko / K.K. / K.K.]-805L, with steric exclusion chromatography, number average molecular weight Mn and weight average molecular weight Mw were measured, and molecular weight distribution were computed from the formula of Mw/Mn. Measurement was proofread using standard polystyrene, using THF as an eluate.

[0022] (2) Heat a bromine content sample with a fuming nitric acid in a well-closed container, it was made to decompose, and quantitative analysis of the generated hydrobromic acid was carried out using the approach (Carius method) of titrating with a silver nitrate.

[0023] (3) Hue (APHA)

The obtained bromination polystyrene was dissolved in the 50ml methylene chloride after 0.10g weighing capacity, and the hue of this solution was measured as compared with the HAZEN standard color solution. It is shown that a hue is so good that a value is small.

[0024] In the glass flask of 5L equipped with [example 1] stirring equipment, reflux equipment, the thermometer, and the tap funnel, dichloromethane 1.68L, 20,000 and a molecular weight distribution Polystyrene (PSt1) 360g of 2.5,

[number average molecular weight] After adding 9.7g of aluminum chlorides which passed the screen of 32 micrometers of apertures (polystyrene solution concentration is 14.0 % of the weight), 1.46kg (it is 2.64 mols to one mol of styrene frame units) of bromines was dropped over 1 hour so that it might maintain at the internal temperature of 5-15 degrees C. Gelation did not take place to bromination reaction time. After ripening the reaction for after [dropping termination] 40 minutes and rinsing a resultant, the dichloromethane layer was dropped at warm water and the solid-state of bromination polystyrene was obtained. It analyzed about this obtained bromination polystyrene, and that evaluation result was shown in Table 1. The solution concentration of bromination reaction time was 14.0 % of the weight, and it excelled in productivity, and the bromine content of the obtained bromination polystyrene was 67.5 % of the weight, and 10 and the hue of APHA were also good.

[0025] 1.81L use of [example 2] dichloromethane was done, and bromination polystyrene was obtained by the same approach as an example 1 except having used 11.8g of 3 ferric chloride which passed the screen of 32 micrometers of apertures instead of the aluminum chloride as a catalyst. The evaluation result of the obtained bromination polystyrene was shown in Table 1.

[0026] Bromination polystyrene was obtained by the same approach as an example 1 except having used mixture (9.8g of aluminium bromide which passed the screen of 32 micrometers of apertures instead of the aluminum chloride as a [example 3] catalyst, and metal aluminum 0.98g which passed the screen of 32 micrometers of apertures). The evaluation result of the obtained bromination polystyrene was shown in Table 1.

[0027] Bromination polystyrene was obtained by the same approach as an example 1 except having used 1.06kg (BrCl) (it being 2.64 mols to one mol of styrene frame units) of bromination chlorine instead of the bromine as a [example 4] brominating agent. The evaluation result of the obtained bromination polystyrene was shown in Table 1.

[0028] Bromination polystyrene was obtained by the same approach as an example 1 except having used 1,2-dichloroethane 1.77L instead of dichloromethane as a [example 5] solvent. The evaluation result of the obtained bromination polystyrene was shown in Table 1.

[0029] As [example 6] raw material polystyrene, number average molecular weight used 11,000, the molecular weight distribution used 555g (PSt2) of polystyrene of 2.4 instead of PSt1, (polystyrene solution concentration is 20.0 % of the weight), and 2.25kg (it is 2.64 mols to one mol of styrene frame units) of bromination polystyrene was obtained for the aluminum chloride which passed the screen of 32 micrometers of apertures by the same approach as an example 1 using 15.0g and a bromine. The evaluation result of the obtained bromination polystyrene was shown in Table 1.

[0030] Bromination polystyrene was obtained by the same approach as an example 1 except having used the aluminum chloride with a mean particle diameter of 40 micrometers (it having asked for mean particle diameter from the particle size distribution by sieving) which has not sifted out as a [example 7] catalyst. Although APHA of the bromination polystyrene obtained by this example fell slightly compared with the bromination polystyrene obtained in the example 1 and the hue was a little inferior, the bromination polystyrene which has high bromine content was obtained. These evaluation results were shown in Table 1.

[0031] In the glass flask of 5L equipped with [example 1 of comparison] stirring equipment, reflux equipment, the thermometer, and the tap funnel, dichloromethane 1.68L, 22,000 and a molecular weight distribution Polystyrene (PSt3) 360g of 3.2, [number average molecular weight] After adding 9.7g of aluminum chlorides which passed the screen of 32 micrometers of apertures (polystyrene solution concentration is 14.0 % of the weight), When 1.46kg (it is 2.64 mols to one mol of styrene frame units) of bromines was dropped over 1 hour so that it might maintain at the internal temperature of 5-15 degrees C, gelation took place.

[0032] 1.81L use of the [example 2 of comparison] dichloromethane was done, and except having used 11.8g of 3 ferric chloride which passed the screen of 32 micrometers of apertures instead of the aluminum chloride as a catalyst, when the bromination reaction was performed like the example 1 of a comparison, gelation took place.

[0033] Except having used mixture (9.8g of aluminium bromide which passed the screen of 32 micrometers of apertures instead of the aluminum chloride as a [example 3 of comparison] catalyst, and metal aluminum 0.98g which passed the screen of 32 micrometers of apertures), when the bromination reaction was performed like the example 1 of a comparison, gelation took place.

[0034] Except having used 1.06kg of bromination chlorine instead of the bromine as a [example 4 of comparison] brominating agent, when the bromination reaction was performed like the example 1 of a comparison, gelation took place.

[0035] Except having used 1,2-dichloroethane 1.77L instead of dichloromethane as a [example 5 of comparison] solvent, when the bromination reaction was performed like the example 1 of a comparison, gelation took place.

[0036] As [example 6 of comparison] raw material polystyrene, instead of PSt1, number average molecular weight used 11,000, the molecular weight distribution used 998g (PSt2) of polystyrene of 2.4, and using 26.9g of aluminum

chlorides and 4.04kg (it is 2.64 mols to one mol of styrene frame units) of bromines which passed the screen of 32 micrometers of apertures, when the dichloromethane solution of 31.0 % of the weight of polystyrene solution concentration performed the bromination reaction like the example 1, gelation took place.

[0037] As [example 7 of comparison] raw material polystyrene, instead of PSt1, number average molecular weight uses 6,000 and a molecular weight distribution uses 555g (PSt4) of polystyrene of 2.2 (polystyrene solution concentration is 20.0 % of the weight). When 2.25kg (it is 2.64 mols to one mol of styrene frame units) of bromination reactions was performed for the aluminum chloride which passed the screen of 32 micrometers of apertures by the same approach as an example 1 using 14.9g and a bromine, gelation did not take place but obtained bromination polystyrene. Although the obtained bromination polystyrene had high bromine content, APHA was set to 30 and the hue got worse. These evaluation results were shown in Table 2.

[0038] As [example 8 of comparison] raw material polystyrene, instead of PSt1, number average molecular weight used 140,000, the molecular weight distribution used 303g (PSt5) of polystyrene of 3.5 (polystyrene solution concentration is 12.0 % of the weight), and when 1.23kg (it is 2.64 mols to one mol of styrene frame units) of bromination reactions was performed like the example 1 using 8.2g and a bromine, gelation took place the aluminum chloride which passed the screen of 32 micrometers of apertures.

[0039]

Table 1

		実施例1	実施例2	実施例3	実施例4	実施例5	実施例6	実施例7
原料ポリスチレン	No.	PSt1	PSt1	PSt1	PSt1	PSt1	PSt2	PSt1
	数平均分子量	20,000	20,000	20,000	20,000	20,000	11,000	20,000
	分子量分布	2.5	2.5	2.5	2.5	2.5	2.4	2.5
臭素化反応条件	触媒	AlCl3	FeCl3	AlBr3+Al (10:1重量比)	AlCl3	AlCl3	AlCl3	AlCl3
	触媒ふるい分け	あり	あり	あり	あり	あり	あり	なし
	臭素化剤	Br2	Br2	Br2	BrCl	Br2	Br2	Br2
	溶媒	ジクロロメタン	ジクロロメタン	ジクロロメタン	ジクロロメタン	1,2-ジクロロエタン	ジクロロメタン	ジクロロメタン
	臭素化反応時の溶液濃度(重量%)	14.0	13.0	14.0	14.0	14.0	20.0	14.0
	臭素化反応時の溶液のゲル化	ゲル化なし	ゲル化なし	ゲル化なし	ゲル化なし	ゲル化なし	ゲル化なし	ゲル化なし
得られた臭素化ポリスチレン	臭素含有率(重量%)	67.5	67.4	67.5	67.5	67.5	67.5	67.4
	APHA	10	15	15	15	15	15	20

[0040]

Table 2

	比較例1	比較例2	比較例3	比較例4	比較例5	比較例6	比較例7	比較例8
原料ポリスチレン	No.	PSt3	PSt3	PSt3	PSt3	PSt3	PSt2	PSt4
	数平均分子量	22,000	22,000	22,000	22,000	22,000	11,000	6,000
	分子量分布	3.2	3.2	3.2	3.2	3.2	2.4	2.2
臭素化反応条件	触媒	AlCl3	FeCl3	AlBr3+Al (10:1重量比)	AlCl3	AlCl3	AlCl3	AlCl3
	触媒ふるい分け	あり	あり	あり	あり	あり	あり	あり
	臭素化剤	Br2	Br2	Br2	BrCl	Br2	Br2	Br2
	溶媒	ジクロロメタン	ジクロロメタン	ジクロロメタン	ジクロロメタン	ジクロロメタン	ジクロロメタン	ジクロロメタン
	臭素化反応時の溶液濃度(%)	14.0	13.0	14.0	14.0	14.0	31.0	20.0
	臭素化反応時の溶液のゲル化	ゲル化	ゲル化	ゲル化	ゲル化	ゲル化	ゲル化なし	ゲル化
得られた臭素化ポリスチレン	臭素含有率(重量%)	-	-	-	-	-	67.4	-
	APHA	-	-	-	-	-	30	-

[0041]

[Effect of the Invention] The hue of this invention is good, it is the approach of manufacturing the high bromination polystyrene of bromine content with sufficient productivity, the obtained bromination polystyrene is suitably used as a highly efficient flame retarder for resin, and the industrial effectiveness which does so is exceptional.

[Translation done.]